

The Effect of Tetraethyl Lead on the Rate of Rise of Pressure in Gaseous Explosions

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Gaseous Explosions

VII—Effect of Tetraethyl Lead on Rate of Rise of Pressure^{1,2}

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Explosive mixtures of different types of hydrocarbons were prepared containing varying amounts of tetraethyl lead. The rate of rise of pressure following ignition was determined from pressure-time curves.

The effect of tetraethyl lead was found to be essentially independent of the chemical structure of the fuel, but governed by the type or rate of combustion of the explosive mixture. As the rate of reaction (or rise in pressure) increases, the retarding action of tetraethyl lead disappears and is replaced by an accelerating action on the combustion.

A similar effect was observed upon adding increasing amounts of tetraethyl lead to the mixture. Small amounts of tetraethyl lead tend to retard slow combustion, but larger concentrations of tetraethyl lead showed no retarding action and in many cases a positive accelerating effect.

These actions may be explained on the assumption that the decomposition products of tetraethyl lead are the active agents, and by considering the relative rates of decomposition of tetraethyl lead and of reaction of the explosive mixture.

THE knocking tendency of a motor fuel is apparently dependent, in large measure, upon its autoignition temperature (32, 20) and the rate of rise of pressure accompanying the normal combustion of the explosive mixture (5). For this reason it seems that important information

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concerning the action of tetraethyl lead in suppressing engine knock may be obtained by investigating its effect, in various concentrations, on the ignition temperatures and on the rates of rise of pressure of different explosive mixtures. The subject of the ignition temperatures of fuels has for some time received a great deal of attention, and considerable data on the effect of tetraethyl lead on ignition temperature are available.

Dixon and Coward (12) studied igniting temperatures of gases in 1909. Probably the earliest determinations on combustible liquids were made by Holm (24) using a heated porcelain plate upon which he dropped the fuels. Seeking to explain the knocking characteristics of fuels on the basis of their ignition temperatures, Moore (32) developed an improved modification of Holm's method which has been widely adopted by later investigators.

The fact that these investigations showed that non-knocking fuels possessed high ignition temperatures led to numerous investigations of the effect of knock suppressors, such as tetraethyl lead, on the ignition temperatures of fuels.

Shortly after the discovery of antiknock compounds by Midgley and Boyd (31), Ricardo (40) stated that these compounds had no effect on the rate of flame propagation or upon the self-ignition temperatures of fuels. Weerman (44), using an apparatus similar to Moore's (32) but with larger combustion space, determined the effect produced by a number of materials on the ignition temperature of petrol. Compounds that have a knock-suppressing action were found to raise the ignition temperature. Using two concentrations of the antiknock material in the same fuel, Weerman found the larger concentration to produce the greater rise in ignition temperature. In the case of tetraethyl lead 0.5 gram per liter of petrol (1.14 cc. per gallon) raised the ignition temperature 105° C., and 1.0 gram per liter (2.28 cc. per gallon) raised the ignition temperature 130° C. Other concentrations of the antiknock in petrol were not reported.

Masson and Hamilton (28) reported the autoignition temperatures, determined by Moore's method, of a large number of substances and mixtures, and indicated that the effect of tetraethyl lead in increasing proportions differed with different fuels. The ignition temperature of *n*-heptane (451° C.) was rapidly increased by the addition of tetraethyl lead, apparently reaching a maximum of about 545° C. by the addition of 8 cc. of tetraethyl lead per gallon. The addition of 62 cc. per gallon also gave 545° C. The ignition temperature of benzene, on the other hand, was found to decrease from about 650° C. to 630° C. as the tetraethyl lead was increased from zero to 5 cc. per gallon. Further additions up to 45 cc. per gallon caused it to rise above the minimum and nearly to the temperature given for the pure substance. The ignition temperature of alcohol (550° C.) decreased rapidly with small additions of tetraethyl lead, reaching about 500° C. at 5 cc.

per gallon. Further additions caused a similar but less pronounced change as the ignition temperature was reduced to almost 475° C. by the addition of 45 cc. per gallon.

n-Heptane, as a fuel, has decided knocking tendencies which are decreased by the addition of tetraethyl lead, apparently accompanied by an increase in the ignition temperature. Benzene and alcohol, strictly non-knocking fuels, have their ignition temperatures lowered by the addition of tetraethyl lead. In fact, the ignition temperature of alcohol treated with tetraethyl lead is apparently lower than that of *n*-heptane treated with a like amount of tetraethyl lead.

Egerton and Gates (19) and other investigators have concluded that the igniting temperatures of fuels are raised by the addition of those compounds known as knock suppressors. However, except for the work of Hamilton and Masson, no data have been reported on the effect of increasing the proportion of tetraethyl lead in the fuel, throughout a wide range of concentrations.

Although the results of work on the effect of tetraethyl lead on the ignition temperatures of fuels have not yet reached satisfactory agreement, the work in that direction has progressed somewhat more rapidly than the investigation of the effect of tetraethyl lead on the velocity of flame travel and the rate of rise of pressure.

Brown and Watkins (4) showed that the velocity of flame propagation and the rate of rise of pressure are similar and are governed by similar conditions. Watkins, in some unpublished work, reported that the maximum rate of rise of pressure decreased for most pure fuels, including normal paraffins, aromatics, and alcohols, upon the addition of 3 cc. per gallon tetraethyl lead, but increased in the case of ether. This apparent contradiction is explained later in the present work.

Egerton and Gates (20, 22) stated that tetramethyl lead and tetraethyl lead delayed the rate of combustion in weak pentane-air mixtures.

Maxwell (29) said that the addition of tetraethyl lead did not affect the rate of inflammation (non-detonating combustion) of paraffin-air mixtures in closed vessels at normal initial temperature and pressure. He quoted Dixon (11) in support of this conclusion. He also cited Egerton (15) as carrying out experiments under conditions in which tetraethyl lead would be expected to decompose, and finding that the decomposition products, if formed, had no apparent effect on the detonation.

Maxwell and Wheeler (30) found that the addition of tetraethyl lead in the ratio of 2.5 fluid ounces per gallon (about 1.2 per cent by volume) caused violent "pinking" in a pentane-air mixture at normal initial temperature and 2 atmospheres initial pressure. Photographs showed violent flame movement and a simultaneous pressure curve showed extremely rapid vibrations. They further demonstrated that if the

tetraethyl lead was decomposed and injected into the bomb just before ignition of the charge, the flame front was smoothed out so as to be almost obliterated and the vibrations were completely removed from the pressure curve.

Laffitte and Dumanois (26) reported experiments with various explosive mixtures and initial pressures ranging from 1 to 7 atmospheres and found that tetraethyl lead did not affect the velocity of the detonation wave once it was initiated.

Aubert, Dumanois, and Pignot (1) found that 5 per cent tetraethyl lead in a hexane-air mixture (1:17.52 by weight fuel-air ratio) increased the duration of the rise of pressure from 0.004 second to 0.011 second.

Duchene (14), using a hexane-air mixture at 80° C., observed detonations which were weakened or eliminated when 5 per cent of tetraethyl lead was added. Duchene (13) also stated that tetraethyl lead suppressed the abrupt appearance of luminosity.

The determinations that have been made on the effect of tetraethyl lead on the rate of rise of pressure have not been evaluated quantitatively and have not included the effect of increasing the concentration of the antiknock compound in the fuel. Therefore, a systematic study of the effect of tetraethyl lead, in varying proportions, in pure fuels, was undertaken in the hope that among the different fuels there would be found some regularity of behavior which might be used as a basis for explaining the action of tetraethyl lead in explosive mixtures.

Apparatus

The apparatus used for this investigation has been described (3) except for minor modifications.

PIPET—Fuels were charged into the bomb by means of a Luer Tuberculin Fournier of 1 cc. capacity, graduated in 0.01 cc. and capable of being estimated to 0.005 cc. The syringe was calibrated with distilled water at 20° C. with the needle in place. This was done by drawing up the plunger until the pipet was filled nearly to capacity, inverting and forcing out air bubbles, if any, and then setting the plunger at a given mark. The plunger was then forced to the end of the stroke, discharging the water into a weighing bottle. The weight of the water displaced, corrected to volume of water at 20° C., was taken as the capacity of the pipet at that mark. Check readings were made at each 0.1 cc. graduation and a calibration curve was drawn by plotting as abscissas the volumes discharged in cubic centimeters, against the pipet readings as ordinates. Inasmuch as the displacement of the liquid is positive by means of a plunger, it was not calibrated for each fuel separately, as would be necessary in the case of the ordinary pipet discharging by gravity. The glass plunger was ground to fit accurately so that, with the finger stopping the opening, considerable pressure must be exerted to move the plunger against the air compressed ahead of it. The needle

was pushed through a small cork which just fitted the opening in the charging valve and prevented the loss of fuel by evaporation, or by "blowing back" because of air bubbles entrapped in the charging valve. The syringe type of pipet was adopted because of the necessity of charging accurately very volatile fuels such as ether. It proved very satisfactory.

PRESSURE ELEMENT—The pressure indicator was calibrated in the manner described (3). In the present work a somewhat stronger spring was used and the pressure was carried up to 1000 pounds per square inch (51,715 mm. Hg) during the calibration.

Fuels Used

The four classes of fuels used were the paraffin hydrocarbons, aromatic hydrocarbons, alcohols, and ether (Table I).

PARAFFINS—The paraffin fuels were *n*-heptane, *n*-octane, and isooctane (isopropyl-tert-butylmethane). The *n*-octane was part of the same sample used by Brown and Watkins (3). This was prepared by Brown and Carr (2) by carefully fractionating straight-run gasoline distilled from Cabin Creek crude. The *n*-heptane and isooctane were obtained from the Ethyl Gasoline Corporation. These were fractionated in a standard column, discarding the first and last cuts of 25 per cent each and keeping only the middle cut of 50 per cent. Further tests of these fuels in a column such as described by Podbielniak (39) showed no detectable amounts of other hydrocarbons.

AROMATICS—The benzene was obtained from the J. T. Baker Chemical Company, chemically pure and thiophene-free. The toluene was part of the sample obtained from the Chemistry Stores by Watkins, whose analysis showed it to be about 99 per cent pure.

ALCOHOLS—The alcohols were methanol and absolute ethyl alcohol. The methanol was obtained from the National Aniline and Chemical Company, absolute and acetone-free. The absolute ethyl alcohol, obtained from the Chemistry Stores, was further purified by refluxing over calcium oxide and carefully fractionating, using the middle cut of 50 per cent.

ETHER—The ethyl ether was obtained from the Mallinckrodt Chemical Works and was chemically pure.

TETRAETHYL LEAD—The tetraethyl lead used was obtained through the courtesy of the Ethyl Gasoline Corporation, whose analysis showed that it contained 98.5 per cent tetraethyl lead. The ethyl fluid sold commercially for mixing with gasolines was not used.

Each fuel was used in the pure condition. Samples of each treated with tetraethyl lead in concentrations of 0.1, 0.2, 0.5, and 1.0 per cent by volume, corresponding to 3.8, 7.6, 18.9, and 37.8 cc. per gallon, were then submitted to the same tests.

EXPLOSIVE MIXTURES—The experiments included two types of explosive mixtures, designated as slow-burning and

fast-burning. The initial conditions within each type were the same for all fuels except ether, as is shown in Table I.

In the slow-burning mixtures oxygen was charged to an absolute pressure of 1050 mm. at 25° C., as shown by a mercury manometer. For the fast-burning mixtures the absolute pressure of oxygen was 1400 mm. at 25° C. The amount of fuel charged in any case was calculated to give a theoretical mixture and the accuracy of charging was checked by complete analyses of the products of combustion after each explosion.

The bomb was purged with nitrogen and, at the time of charging the fuels, was filled with nitrogen at atmospheric pressure. This caused a slight change in the absolute amount of nitrogen present due to changes in the barometric pressure. Throughout the experimental work, however, this variation was less than 0.8 per cent, which was within the accuracy of the pressure gage readings. After charging the oxygen, nitrogen was added to a pressure of 56 pounds per square inch (2900 mm. Hg) at 25° C., as indicated by a pressure gage of the Bourdon type.

The initial temperature of the combustion was 140° C. in all cases. The initial pressure at 140° C. differed slightly with the different classes of fuels, but the variation was in accord with the number of molecules of the fuel necessary to give a theoretical mixture with the absolute amount of oxygen used.

Procedure

The operation of the bomb, the technic involved in obtaining a time-pressure curve, and the analysis of the combustion products have been described (3), but further refinements were made in the method of scaling the time-pressure curves to eliminate from the calculations two possible sources of error: (1) any errors due to differences in the rate of revolution of the drum; and (2) errors due to shrinking or stretching of the photographic paper during development and drying with corresponding changes in the length of the base line. In the present work the r. p. m. of the rotating drum was taken at the time of making each explosion by a combination tachometer and stop watch obtained through the courtesy of Glenn Jewell, of Plymouth, Mich. The stop watch and tachometer were so arranged that by pressing the spindle of the instrument upon the end of the rotating drum shaft the stop watch was released and the tachometer started simultaneously. It was held in position for approximately 30 seconds, during which time the charge in the bomb was fired. Removal of the tachometer spindle from the shaft automatically stopped both watch and counter at the same instant, giving the time accurate to 0.2 second and the number of revolutions of the drum during that time accurate to one revolution. The instrument could then be put aside until the photographic paper was developed and the dark room opened. A typical reading

Table I—Fuels Used
 Nitrogen charged to 56 pounds gage at 25° C.; 52 pounds gage at 10° C. Initial gas in bomb, nitrogen. Temperature fired, 40° C.

FUEL	PHYSICAL CONSTANT			AMOUNT CHARGED					
	B. P. range	Sp. gr. (20°/20° C.)	° C.	SLOW-BURNING			FAST-BURNING		
				Wt.	Vol.	Press. O ₂	Wt.	Vol.	Press. O ₂
Paraffins:				<i>Gram</i>	<i>Cc.</i>	<i>Mm.</i>	<i>Gram</i>	<i>Cc.</i>	<i>Mm.</i>
<i>n</i> -Heptane	98.2	0.6846		0.2088	0.305	1050	0.2875	0.420	1400
<i>n</i> -Octane	124.0-124.3	0.7123		0.2279	0.320	1050		...	..
Isooctane	98.4	0.6939		0.2082	0.300	1050		...	..
Aromatics:									
Benzene	80.0	0.879		0.2288	0.260	1050	0.330	0.375	1400
Toluene	111.0 (99%)	0.860		0.2362	0.284	1050		...	..
Alcohols:									
Methanol	65-67	0.7864 (25/15)		0.5033	0.640	1050	0.6763	0.860	1400
Ethyl	78.4	0.789		0.3629	0.460	1050		...	..
Ether:									
Diethyl	35	0.719 (15/4)		0.2401	0.334	810 (10° C.)	0.3307	0.416	1000 (10° C.)

would be: time, 25.8 seconds; tachometer, 543 revolutions, giving $60/25.8 \times 543 = 1263$ r. p. m.

To overcome the variations noted in the length of the different photographic papers after development and drying, a proportionality method was used. The base line on the photographic paper represented the circumference of the drum. If the number of thousandths of a second required for one revolution of the drum was accurately known, and a line the length of the base line of any given photograph was divided into that number of equal sections, the length of each section, obviously, would represent 0.001 second on the base line of the given photograph. Whether the paper shrank or stretched during the development and drying was immaterial, so long as the base line could be divided into the requisite number of equal sections. Thus for a drum speed of 1250 r. p. m. each revolution required $60/1250 = 0.048$ second. That is, if the base line was divided into 48 equal parts, each section would represent 0.001 second. In practice, it was found more convenient to divide the line into 24 equal parts, each representing 0.002 second. This was done as follows: Taking a sheet of coördinate paper on which a zero line has been designated, one end of the base line of the photograph was placed upon the zero line and the other upon a line of the graph paper 24 equal spaces above the zero line and the points marked. A straight line is drawn between the two points, cutting the 24 equally spaced and parallel lines of the coördinate paper. The distance on this line between any two adjacent parallel lines represents $1/24$ of the base line or 0.002 second for that particular photograph. A pair of spring dividers was set at the length so determined and stepped off along the base line of the photograph to check the accuracy of the setting. Beginning, then, at the instant of recorded pressure rise as the zero abscissa, the dividers were applied to, and points pricked on, the base line below the curve representing the pressure rise. Lines vertical to the base line were then drawn through each of the points, intersecting both the base line and the pressure curve. The distance on the vertical line between the sharply defined top edges of the base line and the curve was measured with a steel scale graduated in 64ths of an inch, and the pressure required to produce this deflection taken from the calibration curve of the pressure element. The pressures were measured directly from the photographic curves at each 0.001 second, plotted to a larger scale, and a smooth curve drawn through the points. Values were read from the plotted curve and the differences were taken as the basis for the differential curve, which was obtained graphically by the method of Running (41).

The maximum pressure and the time required for its development were obtained from the plot of the original time-pressure curve. This maximum pressure, divided by the corresponding time in seconds, gave the average rate of rise and was denoted as $\Delta P/\Delta t$. The maximum rate of rise of

pressure was obtained from the differential curve and was given as maximum dP/dt expressed as pounds per square inch per second.

Results

The experimental work was started on fuel mixtures giving curves of moderate slope which could easily be differentiated graphically (slow-burning mixtures). During the course of the work, for reasons that will develop later, mixtures of greater strength, giving more rapid rates of rise of pressure, were necessary (fast-burning mixtures). Table I gives a list of the fuels with some of their physical constants and the amounts used in the two types of charges.

Although the pressure-time curves such as are shown in Figures 1, 2, and 3 must be consulted to make available all the experimental data, Figures 4 to 12, inclusive, summarize the experimental results obtained with pure fuels and with various additions of tetraethyl lead. Tables II and III indicate the manner in which the data were obtained. Under the Rate of Rise of Pressure are given first the average rate of pressure rise, found by dividing the maximum pressure by the time required to attain it; second, the maximum rate of rise of pressure as found from the differential curve; and third, the time at which the maximum rate was attained as shown by the differential curve. The analyses of the products of combustion as indicated were used largely as a final check on the explosions.

Figure 1 is that of a slow-burning *n*-heptane mixture, plotted to a larger scale and graphically differentiated. Figure 2 is an enlarged pressure-time record of a fast-burning mixture, showing the differential curve. The vibrations shown in the lower part of the curve are present in all the fast-burning mixtures and are due to vibrations in the inflamed gases similar to those previously reported (25). Figure 3 is interesting because it shows the peculiar pressure rise toward the end of combustion accompanying the inflammation of an ether mixture.

For purposes of comparison, the averaged experimental data are plotted in Figures 4, 5, 6, 7, and 8. In the case of all slow-burning mixtures except ether, additions of tetraethyl lead up to 0.1 to 0.2 per cent by volume decrease the maximum rate of rise of pressure. Greater concentrations of lead tend to increase the rate of rise of pressure up to or greater than that of the "undoped" mixture. In all fast-burning mixtures additions of tetraethyl lead increase the maximum rate of rise of pressure. Since all undoped, slow-burning mixtures developed a maximum rate of rise of pressure not exceeding about 50,000 pounds per square inch (2,600,000 mm.) per second, except that of ether, which showed a maximum rate of rise of pressure of 90,000 pounds per square inch (4,650,000 mm.) per second, and all fast-burning mixtures developed a maximum rate of rise of pressure of over 100,000 pounds per

Table II—Effect of Increasing Percentage of Tetraethyl Lead in *n*-Heptane—Slow-Burning Mixtures
(*n*-Heptane, 0.305 cc. Oxygen, 1050 mm. at 25° C.)

RUN	FUEL	MAX. PRESS.	TIME OF MAX. PRESS.	RATE OF RISE OF PRESSURE				ANALYSIS OF COMBUSTION PRODUCTS							
				Av. $\frac{\Delta P}{\Delta T}$	Max. $\frac{dP}{dT}$	Time of $\frac{dP}{dT}$		CO ₂	C _n H _m	O ₂	CO	H ₂	CH ₄	N ₁	
						max.	$\frac{dP}{dT}$								
<i>Lbs./sq. in. Sec.</i>															
144	<i>n</i> -Heptane	558	0.020	27,900	45,600	0.0150	18.1	0.0	2.3	0.0	0.0	0.0	0.0	79.6	
145	<i>n</i> -Heptane	556	0.020	27,800	44,400	0.0146	18.6	0.0	2.1	0.0	0.0	0.0	0.0	79.3	
163	<i>n</i> -Heptane	596	0.021	28,500	44,800	0.0142	19.2	0.0	0.8	0.0	0.0	0.0	0.5	79.5	
164	<i>n</i> -Heptane	556	0.020	27,800	44,600	0.0152	19.3	0.0	1.3	0.0	0.0	0.0	0.5	78.9	
165	<i>n</i> -Heptane	542	0.020	27,100	44,800	0.0132	19.3	0.0	0.8	0.0	0.0	0.0	0.4	79.5	
<i>n</i> -Heptane + PbEt ₄															
% by vol.															
150	0.077	590	0.020	26,800	41,800	0.0156	17.7	0.2	1.9	0.2	0.2	0.0	0.0	79.8	
151	0.077	596	0.0225	25,500	41,400	0.0152	18.4	0.0	2.3	0.0	0.0	0.0	0.4	78.9	
154	0.10	584	0.0230	25,400	41,200	0.0150	18.4	0.0	1.2	0.0	0.0	0.0	0.0	80.4	
155	0.10	584	0.0230	25,400	41,400	0.0156	19.1	0.2	1.7	0.0	0.2	0.2	0.2	78.6	
156	0.20	584	0.0230	25,400	40,400	0.0150	19.0	0.2	1.4	0.2	0.0	0.0	0.2	79.0	
157	0.20	570	0.0230	24,800	38,800	0.0184	17.9	0.0	2.1	0.0	0.0	0.0	0.0	80.0	
251	0.50	554	0.0190	29,100	43,000	0.0150	18.1	0.0	2.3	0.0	0.0	0.0	0.0	79.6	
252	0.50	558	0.0190	29,400	43,400	0.0131	18.6	0.0	2.1	0.0	0.0	0.4	0.2	78.7	
253	0.50	567	0.0197	28,800	42,600	0.0153	18.1	0.0	1.9	0.0	0.0	0.0	0.0	80.0	
303	1.0	588	0.0210	28,000	47,200	0.0168	18.7	0.0	1.4	0.0	0.0	0.0	0.6	79.3	
304	1.0	590	0.0215	27,400	47,000	0.0173	17.9	0.0	2.1	0.0	0.0	0.4	0.8	79.0	

Table III—Effect of Increasing Percentage of Lead Tetraethyl in *n*-Heptane—Fast-Burning Mixtures
(*n*-Heptane, 0.420 cc. Oxygen, 1400 mm. at 25° C.)

RUN	FUEL	MAX. PRESS.	TIME OF MAX. PRESS.	RATE OF RISE OF PRESSURE				ANALYSIS OF COMBUSTION PRODUCTS						
				Av. $\frac{\Delta P}{\Delta T}$	Max. $\frac{dP}{dT}$	Time of $\frac{dP}{dT}$ max. $\frac{dT}$		CO ₂	C ₂ H ₅ n	O ₂	CO	H ₂	CH ₄	N ₂
278	<i>n</i> -Heptane	724	0.0095	76,200	109,500	0.0069		27.4	0.0	0.8	0.2	0.0	0.8	70.8
279	<i>n</i> -Heptane	715	0.0094	76,100	109,500	0.0076		26.7	0.0	1.4	0.0	0.0	0.0	71.9
	<i>n</i> -Heptane + PbEt ₄													
	% by vol.		Sec.											
280	0.10	709	0.0090	78,800	109,000	0.0070		26.2	0.0	2.3	0.4	0.4	0.0	70.7
281	0.10	728	0.0090	81,000	111,000	0.0070		26.8	0.0	1.9	0.2	0.2	0.0	70.9
282	0.50	731	0.0090	81,200	111,000	0.0071		26.2	0.0	1.8	0.2	0.0	0.2	71.6
283	0.50	725	0.0090	80,600	112,000	0.0071		25.9	0.0	1.8	0.0	0.0	0.0	72.3
284	0.50	731	0.0090	81,200	112,000	0.0077		25.9	0.0	0.8	1.4	0.6	0.6	70.7
399	1.0	766	0.0075	102,000	130,500	0.0065		26.6	0.0	1.8	0.0	0.0	0.4	71.2
401	1.0	766	0.0075	102,000	130,000	0.0054		27.3	0.0	1.4	0.0	0.0	0.4	70.9
402	1.0	766	0.0075	102,000	132,500	0.0050		26.6	0.0	1.0	2.0	1.0	0.6	69.8
404	1.0	773	0.0075	103,000	131,500	0.0064		25.5	0.0	0.8	1.8	1.0	0.6	70.3

square inch (5,171,500 mm.) per second, it seemed that the rate of rise of pressure of the undoped mixture might be an important consideration in determining the effect of the tetraethyl lead additions. In Figure 7 the effect of tetraethyl lead appears to be proportionate to the rate of rise of pressure of

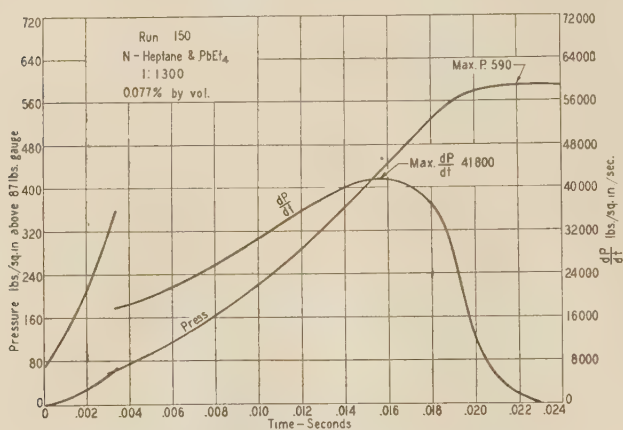


Figure 1

the undoped mixture in the case of alcohol, heptane, and benzene, and would seem to support this conclusion. The fact that ether does not seem to fall in line with the other fuels may be due to some marked difference in the mechanism of combustion of ether.

The paraffin hydrocarbons, the aromatic hydrocarbons, and

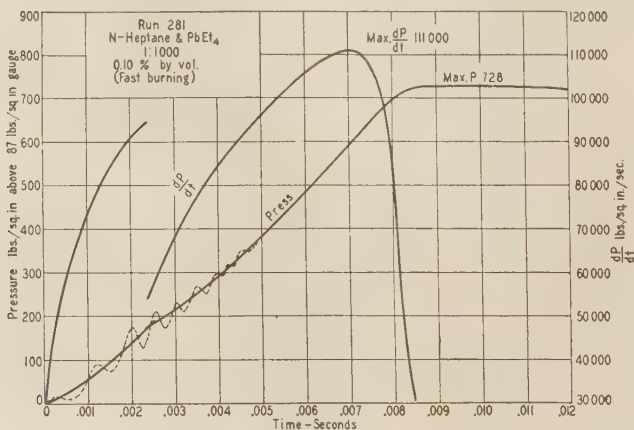


Figure 2

the alcohols, in slow-burning mixtures, produced the same general type of curve, which, when graphically differentiated, showed a gradually increasing rate of pressure rise, reaching a maximum rate just beyond the midpoint of the time-pressure curve.

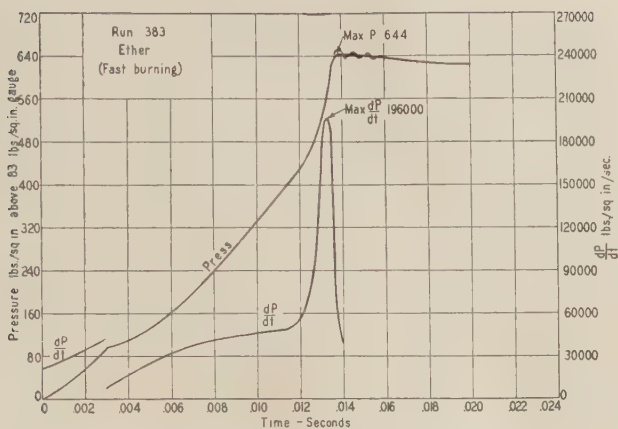


Figure 3

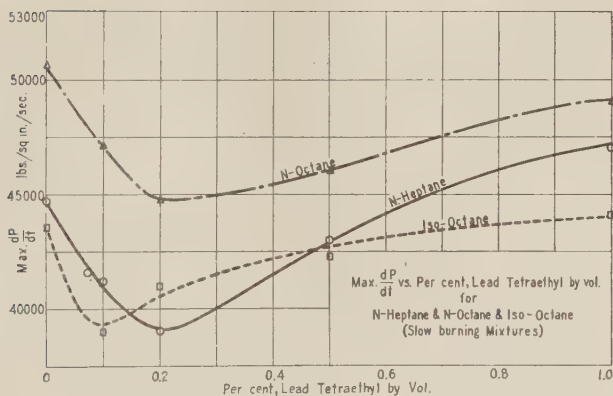


Figure 4

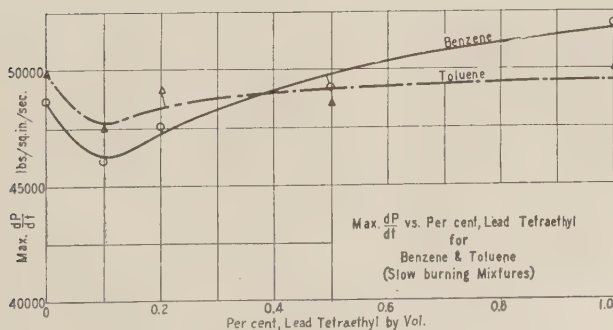


Figure 5

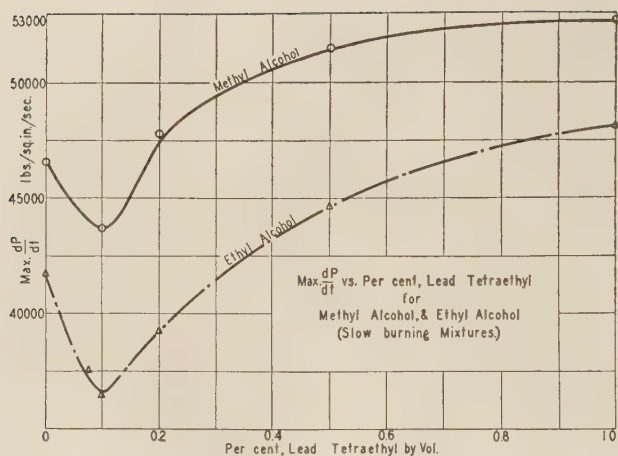


Figure 6

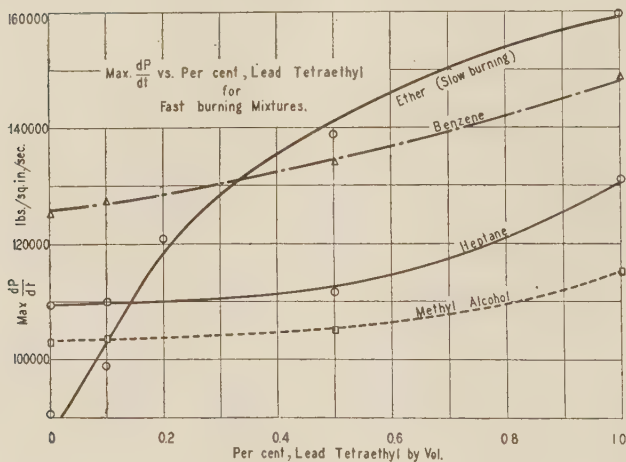


Figure 7

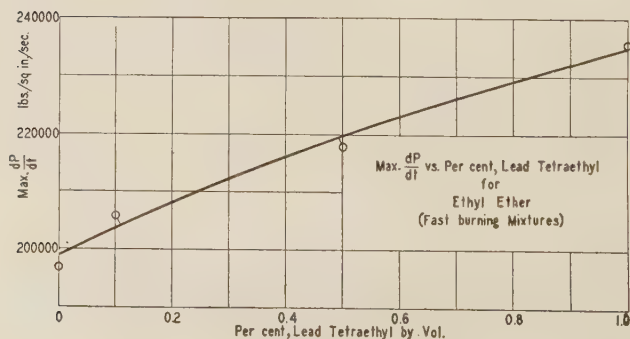


Figure 8

Ether, in slow-burning mixtures, produced a distinctly different type of curve, which seemed to be composed of two distinct successive pressure rises, each with its characteristic rate; the first rise in pressure starting slowly and increasing gradually, similar to that in the other fuel mixtures, followed by a second rise of greater velocity which develops into a very rapid rate of rise of pressure near the end of the curve.

These considerations led to an examination of the earlier portion of the ether curve, where the rate of pressure rise was below the maximum rates of the other fuels. A small section of these rate (derived) curves was plotted to an enlarged scale in Figure 9. Data read from these curves at different time intervals were plotted as a function of tetraethyl lead concentration in Figure 10. In this plot it is evident that the effect of tetraethyl lead on ether is similar to its effect on other fuels

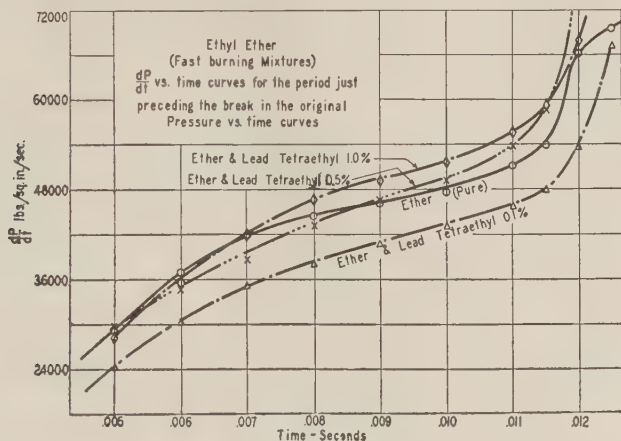


Figure 9

when the rates of rise of pressure are of the same magnitude. It is also interesting in Figure 9 (see also Figures 7 and 8) to note that the retarding action of lead is more pronounced the slower the rate of rise of pressure and that the accelerating action is more pronounced the higher the rate of rise of pressure.

It was noteworthy also that in the fast-burning ether mixtures, which were on the verge of setting up vibrations at the end of combustion, additions of tetraethyl lead caused successively greater vibration at the top of the curve. This is in agreement with similar data obtained by Maxwell and Wheeler (80) on the effect of tetraethyl lead on pentane-air mixtures.

These data indicate that the tetraethyl lead had one effect for rates of pressure rise below 60,000 pounds per square inch (3,100,000 mm.) per second, and a different effect for rates above 90,000 pounds per square inch (4,650,000 mm.) per second. Fortunately, the rate curves obtained for the fast-

burning mixtures of *n*-heptane gave a means of comparison for the range beginning at about 60,000 and extending beyond 90,000 pounds per square inch per second. The rate curve of *n*-heptane was plotted (Figure 11) in the manner described for the slow-burning portion of the ether curves. Beside this was plotted the rate curve for *n*-heptane containing 0.1 per cent of tetraethyl lead by volume. This was below the rate curve for pure *n*-heptane at 60,000 pounds per square inch per second, but gradually converged upon it, until, at about 97,000 pounds per square inch per second, the curves crossed. The rate curve for *n*-heptane containing 0.5 per cent of tetraethyl lead was above the curve for the pure heptane throughout its length, and the rate curve for the *n*-heptane containing 1.0 per cent of tetraethyl lead was considerably above all the other rate curves until it passed its maximum. This maximum was reached in a shorter time than were the maxima of the other curves, indicating that the combustion of the charge required less time when tetraethyl lead was present in the larger amounts.

Considering the rate curves of Figure 11, if at a time preceding the point at which they converge, as at 0.003 second, the rate values are read from their respective curves in the order of the increasing percentage of tetraethyl lead and plotted against per cent of tetraethyl lead as abscissas (Figure 12), the form of the curve is similar to that obtained with any slow-burning mixture. At points later than the time of convergence of the curves, as at 0.006 second, a curve obtained in a similar manner resembled the curves for all fast-burning mixtures. This was further evidence that there is a critical rate which must be taken into account when describing the effect of tetraethyl lead on the rate of rise of pressure.

It should be kept in mind that the rates of pressure rise, as given in this paper, have been obtained using a particular type of bomb and certain well-defined initial conditions of temperature, pressure, and strength of charge. Therefore, these numerical values, given for the sake of making the discussion definite as regards this work, should not be considered as absolute values for all experiments of this kind, some of which will involve the use of other types of apparatus and entirely different conditions.

Conclusions Based on Experimental Work

1—The effect of adding tetraethyl lead to explosive mixtures is essentially independent of the chemical structure of the fuel—viz., paraffin hydrocarbons, aromatic hydrocarbons, alcohols, and ether—differing only in degree for the different classes of fuels, but is largely governed by the type or rate of the combustion following ignition.

2—For mixtures which give a maximum rate of rise of pressure below a critical rate (approximately 90,000 pounds per square inch per second in this work), the effect of small amounts of tetraethyl lead (0.1 to 0.2 per cent by volume) is

to decrease the maximum rate of rise; greater additions tend to increase the maximum rate of rise of pressure in some cases above that for the untreated fuel.

3—For mixtures which give a maximum rate of rise of pressure above the critical rate, the effect of tetraethyl lead, at least in proportions from 0.1 to 1.0 per cent by volume, is to increase the maximum rate of rise with all fuels tested.

4—When the rates of pressure rise are taken from the same curves, above and below the critical rate, as was done with ether and fast-burning *n*-heptane, the effect of the tetraethyl lead on each side of the critical rate is consistent with its effect on the maximum rates which are above or below the critical point.

5—The effect of tetraethyl lead on the rate of rise of pressure is dependent upon the normal rate of rise of pressure of the fuel mixture, and is at least qualitatively independent of the chemical composition of the fuel.

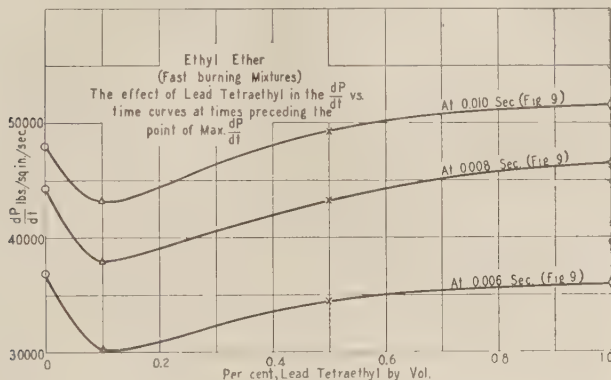


Figure 10

Theoretical Discussion

Although a full discussion of the mechanism by which tetraethyl lead influences combustion is out of the question because of incomplete information, the consideration of previous work with data presented above clearly indicates that the effect of tetraethyl lead upon gaseous explosions is due to the presence of its decomposition products, which in turn is dependent upon the relative rate of decomposition of tetraethyl lead and the rate of rise of pressure, or more probably the rate of reaction and release of energy, of the explosive mixture.

Egerton and Gates (18) found that decomposition of tetraethyl lead in the vapor phase started at 230° C. but was not complete until the temperature had been raised to above a "red heat." A yellowish white intermediate product formed at about 400° C. and sublimed onto the cooler portions of the tube. This product ignited with a flash of blue flame and the

formation of a dark gray deposit at a red heat. The decomposition products formed at 230° C. were practically without effect on the rate of inflammation of explosive mixtures.

Maxwell and Wheeler (30) recorded flame photographs and pressure curves of pentane-air mixtures containing 3.8 per cent of pentane at 15° C. and 2 atmospheres pressure with the following results:

(1) Pentane-air, untreated, gave a slight "pinking," some turbulence of flame front, and vigorous vibration of the pressure indicator curve.

(2) Pentane-air, with tetraethyl lead (1.18 per cent), gave a decided pinking, extreme turbulence of the flame and violent displacement of the pressure curve. (The mirror of the optical indicator was thrown from its seating.)

(3) Pentane-air, with the tetraethyl lead thermally decomposed before ignition, gave no pinking, nearly obliterated the flame front, and showed a very regular rise of pressure.

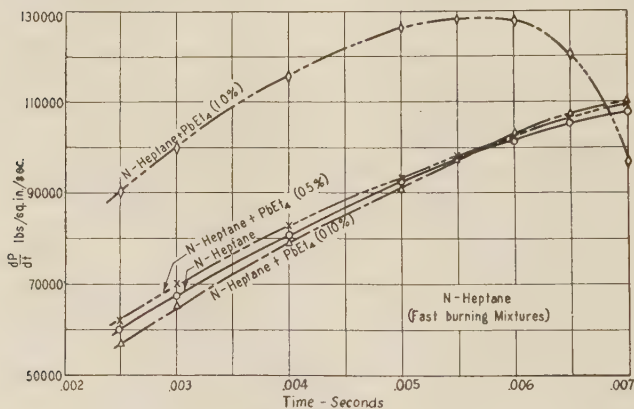


Figure 11

They reasoned, therefore, that it is the decomposition products of tetraethyl lead that have the depressing action on the flame velocity and rate of rise of pressure, in the third type of mixture.

The second type is equivalent to our slow-burning mixture containing over one per cent of tetraethyl lead, and accordingly showed a rate of rise of pressure greater than that of the untreated mixture. (Figure 4)

An explanation for the varying action of tetraethyl lead depending upon the rate of rise of pressure of the explosive mixture involves the assumption that the decomposition products of tetraethyl lead are the active agents in retarding the rate of inflammation and rise of pressure. The data obtained by Maxwell and Wheeler (30) justify this assumption.

In slow-burning mixtures the rate of inflammation may be considered sufficiently slow to allow sufficient of the tetraethyl lead vapor to decompose to that extent necessary to retard

inflammation, before the reaction develops its maximum rate. Adiabatic compressions of the gas ahead of the flame and heat transfer from the burning gases would readily cause decomposition of tetraethyl lead, which starts at 230° C., in a mixture initially at 140° C.

In fast-burning mixtures the rate of inflammation or of reaction may be considered as faster than the rate of decomposition of tetraethyl lead. Under such conditions the decomposition of tetraethyl lead starts in a layer of gas ahead of the flame, but does not have time to form those products which act to retard the flame before the reaction develops its maximum rate. The accelerating action of the tetraethyl lead in the fast-burning mixtures may be due to the explosive action of decomposition which occurs in the flame front or possibly to the positive catalytic action of some intermediate decomposition product such as free ethyl radicals (23).

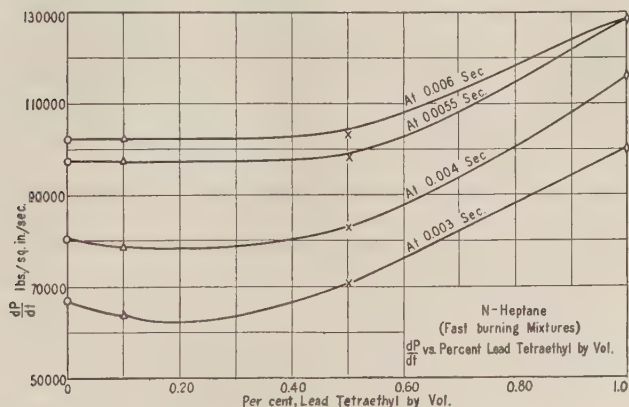


Figure 12

The accelerating action of high percentages of tetraethyl lead and the retarding action of low percentages of tetraethyl lead in slow-burning mixtures also indicate some such double action with one or the other effect predominating, depending upon conditions.

If the proportion of tetraethyl lead is small in slow-burning mixtures, the tetraethyl lead decomposed ahead of the flame front or at least before the maximum rate of reaction is attained is sufficient to reduce the velocity of flame travel and the rate of rise of pressure. The net amount of tetraethyl lead or intermediate products remaining, assuming a definite rate of decomposition of tetraethyl lead for the given conditions, will be small and the accelerating action at the high temperatures in the flame front will not be noticeable.

If the proportion of tetraethyl lead is larger, assuming the same rate of decomposition for the same conditions as for a first order reaction, the net amount of tetraethyl lead or intermediate decomposition products remaining any time to accel-

erate the flame reaction and rate of rise of pressure will be larger, neutralizing the effect of the complete decomposition products. The total effect is to increase the flame velocity and the maximum rate of rise of pressure, in some cases above the normal rate for the fuel mixture.

Pertinent to this conception, there seems to be general agreement that, in order to be effective, the organo-metallic compound must be decomposed. There are also suggestions of a relationship between flame velocity and the effect produced by the tetraethyl lead. Egerton and Gates (21, 22) found that tetraethyl lead reduced the velocity of weak pentane-air mixtures, and Egerton has suggested (17) that the "lack of effect of antiknocks in delaying detonation in a tube or in appreciably affecting the adiabatic ignition temperature is that in such explosions there is so much heat available that the reactions have been auto-accelerated before they can be affected by the inhibitor." This might be interpreted that slow flame movement permits the decomposition of tetraethyl lead to proceed, with the resulting retarding effect of the decomposition products in the unburned charge, whereas the more rapid flame travel develops its maximum rate of reaction before the decomposition products of tetraethyl lead can form or have an effect ahead of the flame.

In this connection the work of Nagai (35, 36) on the effect of tetraethyl lead, tetramethyl tin, and diethyl selenide on the movement of flame in hydrocarbon-air mixtures is of interest. He reports the speed of uniform movement of flame in different air-fuel ratios and increasing amounts of "dope" up to 2 molecular per cent. His data, although limited, clearly indicate the retarding and later accelerating action of the lead and tin compounds when added in increasing percentages. Nagai believes that if the "theoretical flame propagation temperature of the combustible is lower than that of the antiknock compound, the fuel reaction will lose activation energy to the antiknock until the latter is sufficiently activated to burn, when the whole mixture will burn at the higher theoretical flame propagation temperature."

Literature Cited

- (1) Aubert, Dumanois, and Pignot, *Compt. rend.*, **186**, 1298 (1928).
- (2) Brown and Carr, *IND. ENG. CHEM.*, **18**, 718 (1926).
- (3) Brown and Watkins, *Ibid.*, **19**, 280 (1927).
- (4) Brown and Watkins, *Ibid.*, **19**, 363 (1927).
- (5) Brown and Watkins, *Ibid.*, **19**, 366 (1927).
- (6) Church, Mack, and Boord, *Ibid.*, **18**, 334 (1926).
- (7) Clark, *J. Soc. Automotive Eng.*, **23**, 167 (1928).
- (8) Clark, Brugmann, and Thee, *IND. ENG. CHEM.*, **17**, 1226 (1925).
- (9) Collendar, *Engineering*, **123**, 147 (1927).
- (10) Collendar, King, and Sims, *Ibid.*, **121**, 475 (1926).
- (11) Dixon, *Trans. Faraday Soc.*, **1926**, 372.
- (12) Dixon and Coward, *J. Chem. Soc.*, **95**, 514 (1913).
- (13) Duchene, *Compt. rend.*, **186**, 220 (1928).
- (14) Duchene, *Ibid.*, **187**, 200 (1928).
- (15) Egerton, *Nature*, **119**, 259 (1927).
- (16) Egerton, *J. Inst. Petroleum Tech.*, **14**, 662 (1928).
- (17) Egerton, *Ibid.*, **14**, 665 (1928).

- (18) Egerton and Gates, *Ibid.*, **13**, 244 (1927).
- (19) Egerton and Gates, *Ibid.*, **13**, 273 (1927).
- (20) Egerton and Gates, *Ibid.*, **13**, 281 (1927).
- (21) Egerton and Gates, *Proc. Roy. Soc. (London)*, **114A**, 152 (1927).
- (22) Egerton and Gates, *Ibid.*, **116A**, 516 (1927).
- (23) Gomberg, *J. IND. ENG. CHEM.*, **6**, 339 (1914).
- (24) Holm, *Z. angew. Chem.*, **26**, 273 (1913).
- (25) Hunn and Brown, *IND. ENG. CHEM.*, **20**, 1032 (1928).
- (26) Laffitte and Dumanois, *Compt. rend.*, **186**, 146 (1928).
- (27) Lind and Bardwell, *IND. ENG. CHEM.*, **19**, 231 (1927).
- (28) Masson and Hamilton, *Ibid.*, **19**, 1335 (1927); **21**, 544 (1929).
- (29) Maxwell, *J. Inst. Petroleum Tech.*, **13**, 235 (1927).
- (30) Maxwell and Wheeler, *Ibid.*, **14**, 175 (1928).
- (31) Midgley and Boyd, *J. IND. ENG. CHEM.*, **14**, 894 (1922).
- (32) Moore, *J. Soc. Chem. Ind.*, **36**, 109 (1917).
- (33) Moureu and Dufraisse, *Ibid.*, **47**, 852 (1928).
- (34) Moureu, Dufraisse, and Chaux, *Ann. office nat. comb. liquides*, **2**, 233 (1927).
- (35) Nagai, *Proc. Imp. Acad. (Japan)*, **3**, 664 (1927).
- (36) Nagai, *Ibid.*, **4**, 525 (1928).
- (37) Olin and Jebens, *IND. ENG. CHEM.*, **21**, 43 (1929).
- (38) Olin, Read, and Goos, *Ibid.*, **18**, 1316 (1926).
- (39) Podbielniak, *Oil Gas J.*, **27**, No 35, 38 (Jan. 17, 1929); *Refiner Natural Gasoline Mfgr.*, **8**, 55 (1929).
- (40) Ricardo, Institute of Automobile Engineers, Rept. Motor Fuels Committee, Vol. XVIII, Pt. 1, p. 327.
- (41) Running, *Lefax*, Oct., 1920, p. 1; *Mich. Tech.*, **32**, 41 (1919).
- (42) Sims and Mardles, *Engineering*, **121**, 774 (1926).
- (43) Taylor, *Nature*, **119**, 74 (1927).
- (44) Weerman, *J. Inst. Petroleum Tech.*, **13**, 300 (1927).
- (45) Wendt and Grimm, *IND. ENG. CHEM.*, **16**, 890 (1924).

